PARTIAL MELT PROCESSING OF MAGNETICALLY-ALIGNED $YBa_2Cu_3O_{7-x}$ THICK FILMS

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Abstract -- Textured $YBa_2Cu_3O_{7-x}$ (YBCO) thick films were fabricated in the green state by casting particulate-based suspensions in an applied magnetic field (7 T) at ambient temperature. These films, along with non-aligned films, were fired to various temperatures above the peritectic temperature (≈1020°C) to evaluate the effects of partial melt processing on their microstructural development and performance properties. The degree of domain alignment in the fired films was measured by x-ray diffraction (XRD) analysis. This showed that the aligned films had a high degree of c-axis texture. Examination by SEM/EDAX revealed distinct differences in both the film density and texture development between aligned and nonaligned films. Finally, the magnetic properties of each film were measured at 5 K using a SQUID magnetometer (5.5 T maximum field). These measurements indicated that a high degree of anisotropy was present only in the partial melt processed aligned YBCO films.

I. INTRODUCTION

Since the discovery of high T_c superconductors, there has been a tremendous research effort focused on improving their performance properties for bulk applications. While the current carrying capability of polycrystalline $YBa_2Cu_3O_{7-x}$ (YBCO) can be limited due to the presence of intergranular weak-links, this material has the greatest potential for application at 77 K due to its high flux pinning energy relative to Bi-based and Tl-based compounds [1]. Therefore, several investigators have concentrated on understanding and controlling the chemistry at the grain boundaries and on fabrication of grain-aligned YBCO samples in order to improve their weak-link behavior [2-4].

Melt texturing and magnetic alignment are two of the most promising techniques developed to produce grain-aligned YBCO components. Each technique, however, has certain limitations. Melt texturing, achieved either by a melt growth process [5,6] or by directional solidification [7,8], has produced high performance YBCO samples with transport J_c values above $1x10^4$ A/cm^2 at 77 K in an applied magnetic field of 1 T. The main limitation of melt growth processes is that while individual domains have preferred c-axis orientation, little alignment exists between domains in bulk samples. In contrast, directional solidification processes produce highly oriented bulk components, but the growth rates are extremely slow (≈ 1 μm/sec).

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Several researchers have demonstrated that magnetic field alignment of YBCO particles at ambient temperature produces textured bulk samples [9,10]. However, since these samples are typically sintered below 1000°C, they display inferior transport properties relative to melt processed samples. In fact, the effect of partial melting on YBCO films aligned in the green state has not been previously investigated, though Lees et al. recently coupled these techniques by densifying polycrystalline YBCO *in situ* in an applied magnetic field (1-7 T) at temperatures between 900 - 1060°C [11-13]. While their results suggest that coupling these techniques is beneficial, this approach may not be suitable for producing the large quantities needed in many applications.

In this paper, we describe a novel processing method that combines the advantages of the above techniques to produce highly textured YBCO thick films, but avoids *in situ* thermal processing in an applied magnetic field. These films are fabricated in the green state in an applied magnetic field and are then heated above the peritectic temperature for a relatively short period of time. This promotes melting of the smallest YBCO particles first (i.e., Y123 phase --> Liquid + Y211 phase), while the remaining unmelted particles act as templates for growth as shown in Figure 1.

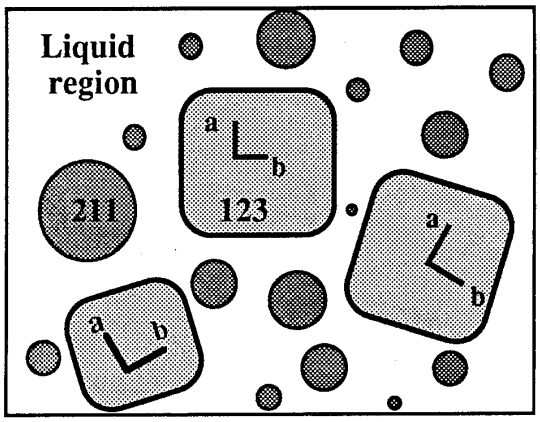

Fig. 1 Schematic representation of partially-melted polycrystalline YBCO, which illustrates the cross-sectional view perpendicular to H_{app}.

Since these particles have been aligned prior to thermal processing, the resulting microstructure should contain domains that are oriented similarly with respect to each other. The objective of our work is to evaluate this method as a

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means of producing aligned, uniform bulk YBCO thick films.

II. EXPERIMENTAL PROCEDURE

YBCO thick films were formed by allowing a particulate suspension to settle in an applied magnetic field (7 T) for 8 hours in ambient conditions. The suspension was made by dissolving an appropriate amount of an organic dispersant (3 wt% based on the weight of YBCO powder) in isopropanol. 10 vol% YBCO powder (SSC, Inc., Woodinville, WA) was added to this solution. The films were cast onto platinum substrates, and their as-dried dimensions were approximately 16.4 mm in diameter and 0.6 mm in thickness. Nonaligned films were cast using identical conditions in the absence of an applied magnetic field. X-ray diffraction (XRD) was used to qualitatively measure the degree of c-axis orientation in the green films.

Both aligned and nonaligned YBCO films were fired to various temperatures (T_{max}) above the peritectic temperature based on the firing schedule shown below in Figure 2.

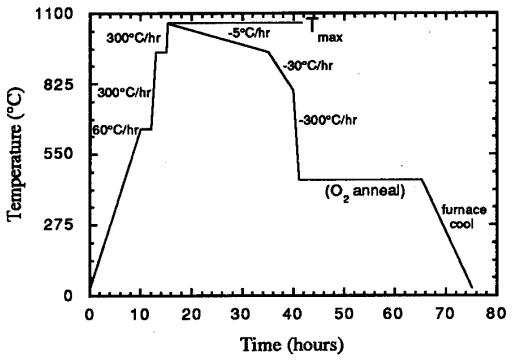


Fig. 2 Heat treatment schedule for YBCO films.

The heat-treated films were analyzed by XRD to determine the degree of c-axis orientation. In addition, scanning electron microscopy (SEM) was used to characterize their microstructural development during densification. Both polished and unpolished cross-sections were evaluated. Finally, magnetic measurements were performed on a high-field (5.5 T maximum) SQUID magnetometer (Model#MPMS2 Quantum Design, San Diego, CA). Samples were oriented with the film surface either perpendicular or parallel to the applied field (H_{app}), which corresponds to H_{app} parallel to c-axis texture ($H_{app} \parallel c$) and H_{app} perpendicular to c-axis texture ($H_{app} \perp c$), respectively. The samples were zero field cooled to 5 K and hysteresis measurements were taken from 0 T to 5.5 T, from 5.5 T to -5.5 T, and back to 5.5 T.

III. RESULTS AND DISCUSSION

XRD analysis of the green YBCO films showed that significant texture was observed in the aligned films relative to the nonaligned films. An orientation factor for the (006) reflection (P_{006}) was calculated for each film to qualitatively describe the degree of c-axis texture present on film surface, as shown in Figure 3. The P_{006} was found to be approximately 0.55 for the aligned green films. For comparison, the orientation factors calculated for the heat treated films are also shown in Figure 3. The texture difference between the aligned and nonaligned films decreased as T_{max} increased, with the greatest difference observed for films fired to 1050°C. This suggests that above 1050°C, almost complete melting of the Y123 particles occurred. The XRD pattern for the 1050°C aligned film, shown in Figure 4, indicates the strong presence of the (00*l*) reflections.

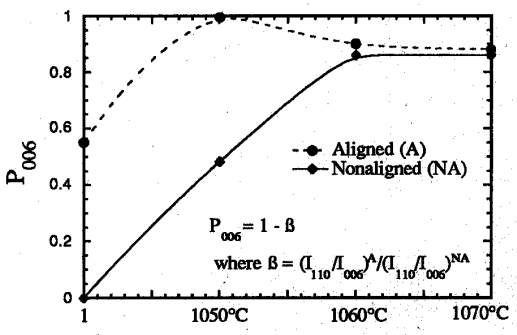


Fig. 3 Preferred orientation factor (P_{006}) as a function of T_{max} for YBCO thick films.

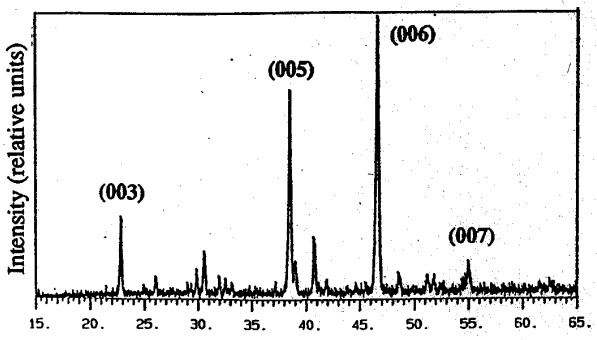


Fig. 4 XRD pattern of an aligned YBCO film fired to 1050°C.

Scanning electron microscopy was used to evaluate the microstructural development in aligned and nonaligned films as a function of heat treatment conditions. SEM micrographs of aligned and nonaligned films fired to 1050°C are shown in Figure 5a and 5b, respectively. Dramatic differences in the film density, grain size, and texture

development were observed. Large voids and elongated grains were present in the nonaligned film, whereas the aligned film was nearly 100% dense and contained highly textured domains as shown in Figure 6.

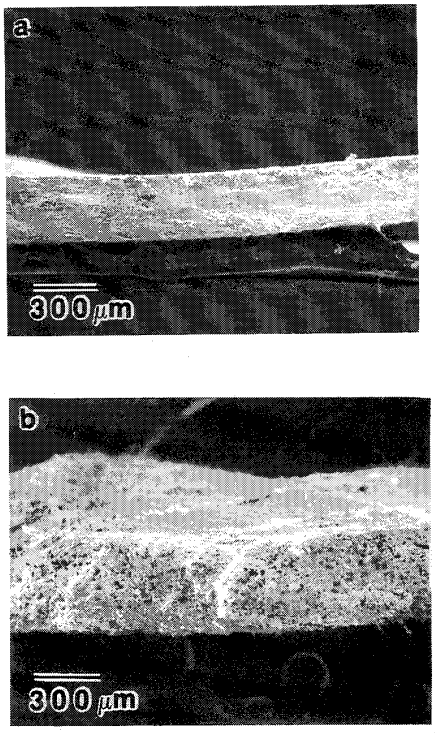


Fig. 5 SEM micrographs of fractured cross-sections of films heated to 1050°C: (a) magnetically aligned film, and (b) nonaligned film.

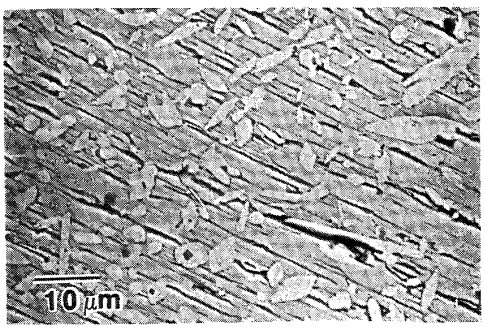
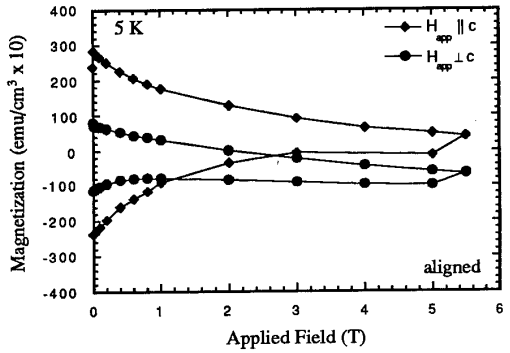


Fig. 6 SEM micrograph of the polished cross-section of a magnetically aligned film heated to 1050°C.

The differences in grain size and morphology between these samples result from their initial alignment. It is well known that the a-b directions are fast growth directions upon recrystallization of the Y123 phase. In the nonaligned sample, elongated grains will grow randomly during solidification. However, in the aligned sample, grains (or domains) grow preferentially in the plane parallel to the film surface. Thus, their growth can be constrained by neighboring domains. The domains present in the 1050°C aligned film appear to be isolated from one another by an unreacted barium and copper rich liquid phase. This suggests that these samples were cooled too quickly through the peritectic temperature. In general, the alignment between domains was observed to be better in the 1050°C aligned film than in either aligned or nonaligned films processed at higher temperatures. However, it was not nearly as uniform as the XRD analysis of their top surfaces indicated.

The magnetic properties of both aligned and nonaligned films were measured by a high-field SQUID magnetometer. The results of hysteresis measurements (normalized w.r.t. sample volume) at 5 K for films heated to 1050°C are shown in Figure 7.



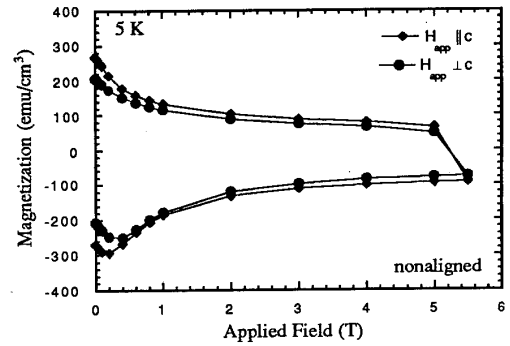


Fig. 7 Magnetization hysteresis loops at 5 K of YBCO thick films heated to 1050°C: (a) magnetically aligned film and (b) nonaligned film.

The hysteresis is strongly anisotropic for the 1050°C aligned film, whereas it is much weaker in the nonaligned film. The degree of anisotropy, defined as the ratio of ΔM ($H \| c$) and ΔM ($H \perp c$) at 1 T, is shown in Figure 8 for each film

as a function of maximum temperature. A maximum anisotropy of 2.45 was observed for the 1050°C aligned film. The difference in anisotropy between aligned and nonaligned films decreased as T_{max} increased, further demonstrating the deleterious effects of complete melting of Y123 particles during heat treatment. In comparing our results to those reported previously by Bourgault et al., they found a maximum anisotropy ratio of 2.9 for bulk samples heated to 1050°C *in situ* in an applied field of 7 T [12]. Other values in the literature for magnetically aligned samples are higher; for example, a value of 5.45 at 4 T was reported for magnetic filter-pressed samples fired to 950°C [10]. Clearly, there is little difference between the texture produced in our films and those densified *in situ* in an applied field. However, thermal processing above the peritectic temperature appears to reduce texture development relative to conventionally sintered aligned YBCO. Yet, the potential advantages of melt processing on performance properties may outweigh this effect.

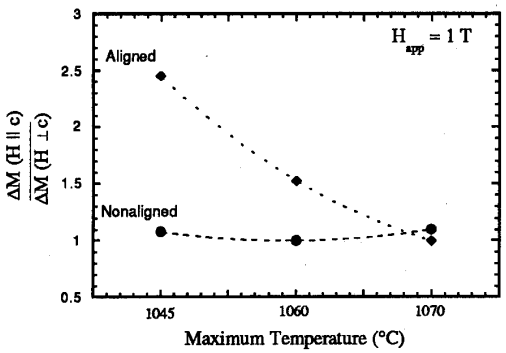


Fig. 8 The variation in anisotropy as a function of maximum temperature for both aligned and nonaligned films.

Another feature of this magnetization study is the variation observed in the magnitude of ΔM, which is generally lower in the aligned films than in the nonaligned films processed at the same temperature. The difference in ΔM (H ∥ c) was greatest for the 1050°C films, and this decreased substantially with increasing temperature. Based on the fast cooling rate employed in this study, this trend is not unexpected since the domains in the aligned films appear to be smaller than the grains in the nonaligned films and somewhat isolated from one another. Future work will focus in part on improving the heat treatment process and the starting particle size distribution of Y123 to achieve greater alignment and improved domain connectivity within these films.

SUMMARY

Partial melt processing of YBCO thick films magnetically aligned in the green state was demonstrated to be an effective approach to fabricating highly textured films. The microstructural development of these films was highly sensitive to the heat treatment conditions. The maximum temperature governed the extent of melting of the Y123 particles, whereas the growth of these particles upon recrystallization appeared to depend on both their orientation as well as the cooling rate. The largest differences between aligned and nonaligned films were observed for those heated to 1050°C. As T_{max} increased, the anisotropy in the magnetic hysteresis measurements and in the preferred orientation factor between the aligned and nonaligned films diminished. The connectivity between domains was poor in the partial melt processed aligned films. However, this can be explained by the fast cooling rates used in this study and improved upon in future work.

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